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BERESKIN & PARR

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Title: A METHOD FOR LOCALLY MODIFYING THE EFFECTIVE BANDGAP  
ENERGY IN INDIUM GALLIUM ARSENIDE  
PHOSPHIDE (InGaAsP) QUANTUM WELL STRUCTURES

Inventor(s): David A. Thompson, Bradley J. Robinson, Gregory J. Letal  
and Alex S. W. Lee

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**FIELD OF THE INVENTION**

This invention relates to quantum well devices and to a method of changing and/or controlling the effective bandgap energy in quantum well structures, particularly Indium Gallium Arsenide Phosphide (InGaAsP) devices or structures. More particularly, it is concerned with enabling the integration of multiple optoelectronic devices within a single structure, each comprising a quantum well structure.

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**BACKGROUND OF THE INVENTION**

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The semiconductor industry is currently interested in integrating various optoelectronic devices, such as lasers, modulators and detectors within a single semiconductor structure. This initiative is motivated by the increasing demand for optoelectronic technology particularly in the optical telecommunications field.

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Integrated optoelectronic devices are of great interest due to the optical alignment and optical coupling efficiency challenges associated with using discrete optoelectronic devices. Within an integrated optoelectronic device, each optical component is spatially self aligned as result of being fabricated within the same semiconductor structure. This inherently gives better transmission between the components of an integrated device, as compared to putting together discrete devices. However, in order to ensure that the separate optical components within the structure each has its own independent characteristics, local modifications to the semiconductor quantum well structure of each component are usually necessary. Many known fabrication techniques for one component of an integrated structure tend to have the unwanted effect of distorting or affecting properties of neighbouring components.

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Quantum Well Intermixing (QWI) is a Post-growth method of

bandgap engineering known in the art, enabling controlled changes in the bandgap energy of selected regions of the quantum well structure. Quantum Well Intermixing uses a Rapid Thermal Annealing (RTA) process also known in the art, to provide controlled diffusion of defects into the  
5 quantum well structure of an optoelectronic device. These defects are usually provided by a layer or layers of specially grown material that are grown above the quantum well structure. Under the influence of the RTA process, the defects diffuse down into the quantum well structure and introduce changes to the bandgap properties. QWI has attracted  
10 considerable interest in locally modifying the quantum well band structure of integrated optoelectronic devices, including tunable wavelength lasers, photodetectors, and modulators. It is believed to be capable of modifying one component with minimum impact on neighbouring components.

Different thermally-driven quantum well intermixing techniques  
15 such as Ion-Implantation Disordering (IID), Impurity Free Defect Diffusion (IFDD), Photo-absorption Induced Disordering (PAID) and Impurity-Induced Layer Disordering (IILD) have been utilized in order to modify the quantum well structure in selected regions.

In Ion Implantation Disordering (IID), high energy implanted  
20 ions may introduce lattice damage to the quantum well structure, resulting in reduced light output. The Impurity-Induced Layer Disordering (IILD) technique requires long anneal times and/or high anneal temperatures (>800 °C) for diffusing impurities into the quantum well region. This can cause undesirable changes in the characteristics of neighbouring  
25 components within an integrated optoelectronic devices. It also introduces unwanted impurities, causing undesirable changes to the properties of the quantum well structure. The Impurity Free Defect Diffusion (IFDD) technique is free of impurities, but control of the QWI process depends on the deposited cap layer being used, it's deposition conditions and the  
30 subsequent thermal anneal treatment. If for example, a silicon dioxide (SiO<sub>2</sub>) cap layer is used, the thermal anneal process requires the use of temperatures between 750-800 °C . These anneal temperatures may

cause an uncontrollable shift in device operating wavelength, such as, the emission wavelength of laser devices. Also, the surface of the grown material may become unstable and therefore unsuitable for subsequent processing of components such as gratings. Furthermore, strain and damage may be introduced to the hetero-structure surface. Finally, Photo-absorption Induced Disorder (PAID) suffers from poor spatial resolution. Consequently, it is difficult to confine this effect to an intended component within an integrated device, without affecting adjacent components.

Accordingly, there is need for a QWI process wherein, surface contamination, uniformity and strain effects are avoided, and which is reproducible. With these characteristics, it should be possible to import desired properties to one component of an integrated structure, without affecting neighbouring components. Furthermore, there is a need for a QWI process that enables the high speed operation of optoelectronic devices, and affects the photo-luminescent properties of the quantum well structure.

### SUMMARY OF THE INVENTION

The present invention discloses a Quantum Well Intermixing (QWI) method for locally modifying the effective bandgap energy in Indium Gallium Arsenide Phosphide (InGaAsP) quantum well structures. This quantum well intermixing method involves growth of a first Indium Phosphide layer with slow diffusing defects grown near the upper quaternary layers of the quantum well structure at normal temperature using Gas Source Molecular Beam Epitaxy (GSMBE). A second Indium Phosphide layer with fast diffusing defects is also grown near the surface of the quantum well structure at normal temperature using Gas Source Molecular Beam Epitaxy (GSMBE). By applying a rapid thermal annealing (RTA) process, both the slow diffusing defects from the first Indium Phosphide layer, and fast diffusing defects from the second Indium Phosphide layer, diffuse to the quantum well active region. This controlled inter-diffusion process provides localised, controlled changes in the properties and bandgap energy of the quantum well active region.

An alternative embodiment to the present invention includes a quantum well intermixing process, wherein an Indium phosphide layer with point defects is grown near the surface of the quantum well structure at low temperature using Gas Source Molecular Beam Epitaxy. By applying rapid thermal annealing (RTA), the point defects in the Indium Phosphide layer  
5 diffuse to the quantum well region. This controlled inter-diffusion process provides an increasingly high effect on the effective bandgap energy of the quantum well active region.

In another aspect of the present invention, quantum well  
10 intermixing is used in order to modify the effective bandgap properties of an integrated optoelectronic device comprising a laser and electro-absorption modulator. The quantum well intermixing process is applied to the electro-absorption modulator region of the integrated optoelectronic device. Following the quantum well intermixing process, the effective bandgap  
15 properties of the Indium Gallium Arsenide Phosphide (InGaAsP) quantum well active region of the modulator are modified. These modifications introduce both an ultra-fast response, and increased efficiency in the operating characteristics of the electro-absorption modulator. This enables the integration of high speed quantum well devices with standard quantum  
20 well devices.

#### **DETAILED DESCRIPTION OF THE DRAWINGS**

For a better understanding of the present invention and to show more clearly how it may be carried into effect, reference will be made  
25 by way of example to the accompanying drawings, in which:

Fig. 1 shows in table form the quantum well structure of an Indium Gallium Arsenide Phosphide (InGaAsP) laser device;

Fig. 2 shows the results of photoluminescence (PL)  
30 measurements for both LT and NT grown InP cap layers, annealed for 30 seconds as a function of temperature;

Fig. 3 shows the result of photoluminescence (PL) measurements for both the LT grown InP layer and the NT grown InP layer, annealed at 725 °C as a function of time;

5            Fig. 4 shows the result of photoluminescence (PL) measurements for both the LT grown InP layer and the NT grown InP layer, annealed at 800 °C, with and without a SiO<sub>2</sub> cap layer;

10           Fig. 5a shows in table form the quantum well structure of an Indium Gallium Arsenide Phosphide (InGaAsP) integrated DFB laser/electro-absorption modulator device;

15           Fig. 5b shows a schematic representation of an integrated DFB laser/electro-absorption modulator device;

20           Fig. 6 shows an experimental graph of the extinction ratio between switching the modulator between the transparency and absorption state.

## 20    **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

25           A quantum well intermixing method is described, wherein the effective bandgap properties of Indium Gallium Arsenide Phosphide (InGaAsP) quantum well structures are modified in order to enable fabrication of high-speed integrated optoelectronic devices. InGaAsP structures operate at emission wavelengths in the region of 1.55µm and 1.3µm, and are particularly used in optoelectronic devices applicable to optical fibre telecommunications. The described method includes process steps based on Gas Source Molecular Beam Epitaxy (GSMBE), patterning/etching and rapid thermal annealing (RTA), for achieving  
30    Quantum Well Intermixing (QWI) in the active region of InGaAsP quantum well structures. It should be appreciated that the GSMBE and RTA processes are known to someone skilled in the art, and are therefore not

described in detail.

Fig. 1 shows an InGaAsP multiple quantum well structure **10** of a laser device. The structure **10** is grown by GSMBE in sequential layers starting from a 5000 Angstrom InP Buffer layer **22** which itself is formed on an n+ InP substrate **11**. The next layer grown on top of the InP buffer layer **22** is an 800 Angstrom 1.15Q guiding layer **18a**. The following layers grown above the guiding layer **18a**, form a conventional quantum well active region **13**, which comprises three quantum well layers **16** and four 1.24Q quaternary layers **17**. The 1.24Q quaternary layers **17** provide barrier regions of higher bandgap energy between the quantum well layers **16**. Optical emissions are generated within this quantum well active region **13**. A second 1.15Q guiding layer **18b** is grown on top of the last quaternary layer **17**. Optical emission generated in the active region **13** is confined between the guiding layers **18a**, **18b** in order to concentrate the optical output emission from the laser device. A 250 Angstrom InP grating layer **14** is grown above the second 1.15Q guiding layer **18b** and used for etching a grating for a Distributed Feed-Back (DFB) laser. A 50 Angstrom InGaAs layer **19** grown above the InP grating layer **14** is used as an etch stop layer. This layer stops the underlying layers (i.e. InP grating layer **14** and quantum well region layers **13**) from being etched away during the removal of the InP defect layer **20**, once the RTA process is complete. The InGaAs layer **19** also preserves the InP grating layer **14** from atmospheric contamination prior to etching the grating. A 1000 Angstrom InP defect layer **20** is grown above the InGaAs layer **19** for the quantum well intermixing process. These defects have been postulated to be donor-like Phosphor-antisites or acceptor-like Indium-Vacancies. During the RTA process, defects in the InP defect layer **20** diffuse into the quantum well region **13**. On completion of the photolithographic/etching and the RTA process, the defect layer **20** is etched away and a thick 1 $\mu$ m layer of InP **21** is grown in its place. A 1000 Angstrom InGaAs contact layer **15** is grown over the 1 $\mu$ m InP layer **21**. The InGaAs layer **15** is a contact layer for applying current to the device. The 1 $\mu$ m layer of InP **21** is normally etched into a ridge structure for confining

and guiding the applied device current from the InGaAs contact layer **15** to a narrow region of the quantum well active region **13**. The  $1\mu\text{m}$  InP layer **21** and the InGaAs contact layer **15** are grown after the RTA process, once the quantum well active region structure **13** has been grown. All layers with the exception of the InP defect layer **20** are typically used in optoelectronic device fabrication. Once the InP defect layer **20** has been used in the quantum well intermixing process in accordance with the present invention, it is removed from the device structure **10**.

The layers of the quantum well structure **10** are grown by GSMBE at a rate of  $1\mu\text{m/hr}$  on a n-type InP substrate **11**. Group V constituent atoms are supplied in the form of  $\text{As}_2$  and  $\text{P}_2$  derived from the pyrolysis of  $\text{AsH}_3$  and  $\text{PH}_3$  in a single, two zone low pressure cracker with a Ta catalyst operating at  $1000^\circ\text{C}$ . All layers except the InP defect layer **20** are grown at  $470^\circ\text{C}$  with the group V total flow rate of 4 or 5 sccm. The InP defect layer **20** is grown at a low temperature (LT) of  $300^\circ\text{C}$  and is referred to as LT-InP. Rapid thermal annealing (RTA) is carried out under a flowing nitrogen ambient, using a halogen lamp rapid thermal annealing system.

In accordance with the present invention, during the RTA process, point defects in the LT-InP defect layer **20** diffuse into the active region **13** of the quantum well structure **10** and modify its composite structure. This controlled inter-diffusion process causes a large increase in the bandgap energy of the quantum well active region **13**. This is referred to as a wavelength blue shift. Applying wavelength blue shift to a selected region of the quantum well active region **13**, increases its transparency, without the need for external biasing. This is due the quantum well bandgap increase which has a higher energy than the generated incident photons. Therefore, the generated photons pass through the transparent quantum well region without being absorbed by electron/hole pairs.

Fig. 2 shows experimental results of photoluminescence (PL) measurements **23** for both Low Temperature (LT) grown InP layer as indicated at **24** and Normal Temperature (NT) grown InP layer as indicated at **25**, annealed at various temperatures in the range  $600\text{-}780^\circ\text{C}$  for 30



seconds. The Low Temperature (LT) and Normal Temperature (NT) grown InP defect layers are referred to as LT-InP and NT-InP respectively. The LT-InP defect layer is grown at 300 °C, whereas the NT-InP layer is grown at 470 °C. Quantum well intermixing is carried out on a NT grown InP defect layer in order to compare the magnitude of wavelength blue shift to that of quantum well intermixed LT grown InP defect layer. The quantum well emission wavelength is determined by room temperature photoluminescence (PL) measurements. The graph 23 shows the changes in quantum well emission wavelength (nm) as the anneal temperature (°C) is increased. Results are shown for both LT (low temperature) and NT (normal temperature) grown InP layers annealed at various temperatures in the range 600-780 °C for 30 seconds. A considerably larger wavelength blue shift ( bandgap energy increase) is achieved for the LT-InP layer, as indicated at 24. At the upper end of the anneal temperature range, at 780 °C, a large wavelength shift of  $\approx 197$  nm is induced by the LT-InP layer as shown at the end of the curve 24, whereas only an  $\approx 35$  nm blue-shift is observed for the NT-InP layer, indicated at 25. The abundance of point defects found in the LT grown InP defect layer causes the large wavelength blue shift, wherein the point defects have been postulated to be donor-like P-antisites or acceptor-like In-vacancies.

Fig. 3 shows the result of photoluminescence (PL) measurements 26 for both the LT grown InP layer, indicated at 28, and NT grown InP layer, indicated at 30, annealed at 725 °C and shown as a function of time. As indicated by the lines 28, 30, both LT grown and NT grown InP defect layers exhibit initial large blue shifts for anneals of only 5 seconds. However, the LT grown InP defect layer, as indicated at 28 gives an  $\approx 71$  nm blue shift which is more than double that of the NT grown InP defect layer, indicated at 30. For a longer anneal time of 60 seconds, the LT grown InP defect layer, indicated at 28, exhibits an  $\approx 132$  nm blue shift, indicated at 34, whereas after 60 seconds the NT grown InP defect layer, indicated at 30, exhibits  $\approx 33$  nm of blue shift, as indicated at 32, in the emission wavelength of the quantum well active region.

Fig. 4 shows the photoluminescence spectra **36** of both the LT grown InP layer, indicated at **46**, and NT grown InP layer, indicated at **40**, **42**, **44**, annealed at 800 °C. For comparison and reference purposes, the spectrum of the quantum well structure as grown and without any quantum well intermixing is shown at **38**. The photoluminescence spectra show the NT grown InP layer which is initially annealed for 60 seconds, as indicated at **40**. This NT grown InP layer exhibits  $\approx 57$  nm of blue shift in the emission wavelength spectrum, compared to the emission wavelength spectrum shown at **38**. Once the NT grown InP layer is capped with a SiO<sub>2</sub> layer (IFDD method) and annealed for 60 seconds, the resulting spectrum, indicated at **42**, shows an  $\approx 142$  nm blue shift in the emission wavelength spectrum, compared to the emission wavelength spectrum, as indicated at **38** of the quantum well region with no quantum well intermixing applied. The most significant blue shift is exhibited by the LT grown InP layer with no SiO<sub>2</sub> capping and annealing time of 60 seconds. The corresponding spectrum **46** shows an  $\approx 230$  nm blue shift in the emission wavelength spectrum compared to the emission wavelength spectrum, as indicated by **38**. Following 180 seconds of anneal time the NT grown InP layer capped with a SiO<sub>2</sub> layer exhibits an  $\approx 214$  nm blue shift in the emission wavelength spectrum, as indicated at **44**, again compared to the emission wavelength spectrum, as indicated at **38**. The results show that even with three times the anneal time (180 seconds) an SiO<sub>2</sub> capped NT grown InP layer does not exhibit as much bandgap blue shift as that of an LT grown InP layer.

The LT grown InP layer exhibits a large bandgap wavelength blue shift in the InGaAsP quantum well region, for relatively short anneal times and lowered anneal temperatures. This is due to the abundance of point defects in the LT grown InP layer. Producing high wavelength blue shift at lower temperatures avoids undesirable effects during growth of integrated optoelectronic devices. For example, an undesirable shift in the emission wavelength of the laser section of an integrated Distributed Feed-Back (DFB) laser/electro-absorption modulator device will occur as a result high temperature anneals.

It will be appreciated that the thickness of the grown InP layer 20 can be varied in order to generate bandgap energy blue shifts over a range of 0-140nm in a single thermal anneal.

Devices that have been grown by MOCVD (molecular chemical vapour deposition) methods can also be bandgap shifted using the low temperature GSMBE grown InP layer and the RTA process.

In an alternative embodiment of the present invention, two defect types are grown for the quantum well intermixing process. Both defect types are grown as individual layers on top of the quantum well active region structure, and diffuse into the quantum well active region following a rapid thermal annealing (RTA) process. One of the diffused defect types generates a bandgap wavelength blue shift in the quantum well active region, resulting in the transparency of this region. The other diffused defect type decreases carrier lifetime in the quantum well active region. This reduction in carrier lifetime enables the InGaAsP quantum well active region to exhibit an ultra high speed response, which is particularly suitable for enabling high speed integrated optoelectronic device fabrication. The following paragraphs describe the growth process and properties of these defect types in more detail.

Referring to Fig. 5a, the InGaAsP quantum well structure is grown on a 5000 Angstrom InP buffer layer 110 which itself is formed on an n+ InP substrate 120. The next layer grown on top of the InP buffer layer 110 is an 800 Angstrom 1.15Q guiding layer 108a. The following layers grown above the guiding layer 108a, form a conventional quantum well active region 103, which comprises three quantum well layers 106 and four 1.24Q quaternary layers 107. The 1.24Q quaternary layers 107 provide barrier regions of higher bandgap energy between the quantum well layers 106. Optical emissions are generated within this quantum well active region 103. A second 1.15Q guiding layer 108b is grown on top of the last quaternary layer 107. Optical emission generated in the active region 103 is confined between the guiding layers 108a, 108b in order to concentrate the optical output emission from the laser device. A first InP defect layer 112 is grown

above the second 1.15Q guiding layer **108b**. This InP layer **112** is grown using a combination of GSMBE and an electron cyclotron resonance (ECR) Helium-Plasma source. During growth, the InP layer **112** is grown under conventional GSMBE conditions, except that the epilayers of the InP **112** are exposed to a flux of helium particles from an ECR source mounted inside the chamber. By exposing the InP layer **112** to the Helium flux, slow diffusing vacancy defects are produced in the InP layer **112**. The thickness of this InP defect layer **112** can be optimized for particular device performance, but successful performance has been demonstrated for a defect layer **112** thickness of 400 Angstroms. A second InP defect layer of 1000 Angstrom thickness **102** is grown at normal temperature (NT-InP) above the first InP defect layer **112**. This defect layer **102** provides fast diffusing group V interstitial type defects. On completion of the photolithographic patterning/etching and the RTA process, the defect layers **102**, **112** are etched away and a thick 1 $\mu$ m layer of InP **114** is grown in its place. A 1000 Angstrom InGaAs contact layer **105** is grown over the 1 $\mu$ m InP layer **114**, wherein the InGaAs layer **105** is a contact layer for applying current to the device. The 1 $\mu$ m layer of InP **114** is normally etched into a ridge structure for confining and guiding the applied device current from the InGaAs contact layer **105** to a narrow region of the quantum well active region **103**. The 1 $\mu$ m InP layer **114** and the InGaAs contact layer **105** are grown after the RTA process, once the quantum well active region structure **103** has been grown. All layers with the exception of the InP defect layers **102**, **112** are typically used in optoelectronic device fabrication. In accordance with this aspect of the present invention, the InGaAs etch stop layer previously shown in Fig. 1 is not grown over the quantum well active region **103** where quantum well intermixing occurs. This is due to the InGaAs etch stop layer obstructing the diffusion of the defects into the quantum well active region **103**.

Once quantum well intermixing is induced by the rapid thermal anneal (RTA) process, the defect types in both the first and second InP defect layers **112**, **102** diffuse into the quantum well active region. The slow

diffusing vacancy defects in the first InP layer **112** diffuse into the quantum well active region **103**, providing deep states that quench the photoluminescence and reduce carrier lifetime within the bandgap. The deep states are intermediate energy levels created within the bandgap of the quantum well active region **103**. These intermediate states suppress radiative transitions within the quantum well active region **103**, by providing an additional carrier transition step during conduction band to valence band carrier recombination. Also, the short transition times of carriers between the valence band and intermediate deep state levels decreases the carrier lifetime. The fast diffusing group V interstitial type defects in the second InP layer **102** diffuse into the quantum well active region **103**, generating a bandgap wavelength blue shift. This causes the quantum well active region **103** to become transparent, permitting incident photons to pass through this region without being absorbed.

The thickness of the first InP defect layer **112** has to be sufficient to supply enough deep states to the quantum well active region **103** whilst allowing enough interstitial defects from the second InP layer **102** to reach the active region **103**. The physical order of the defect layers must also be maintained during GSMBE growth such that the second InP defect layer **102** is grown over the first InP defect layer **112**. This is to ensure that the slow diffusing vacancy type defects in the first InP layer **112**, diffuse far enough into the quantum well active region to produce the deep states. Once the RTA process is complete, the defect layers **102**, **112** are etched away, and current guiding and contact layers **114**, **105** are grown for applying electrical current to the device.

The principal advantage of this aspect of the present invention is identified in fabricating integrated optoelectronic devices, particularly devices comprising an integrated DFB laser and electro-absorption modulator. Fig.5b shows a schematic representation of a fabricated integrated DFB laser/electro-absorption modulator device **48**. Quantum well intermixing using slow diffusing vacancy defects and fast diffusing interstitial defects is applied to the modulator section **52** quantum well active region

**54a**. Firstly, this results in a bandgap blue shift in the modulator section **52** active region **54a** causing the modulator region to be transparent at zero bias. This increases the efficiency of the integrated device **48** due to the optical output signal from the laser passing through the modulator active region **54a** without being absorbed. Second, the existence of deep states within the bandgap of the modulator section **52** active region **54a**, quenches photoluminescence and reduces the carrier lifetime. This causes the modulator **52** to operate at ultra high-speed switching times. By applying a reverse bias voltage to the modulator section **52**, the bandgap of the modulator active region **54a** decreases, causing absorption of the optical signal coupled from the DFB laser section **50**. By removing the reverse bias voltage, the bandgap of the modulator active region **54a** increases back to its original state and the modulator active region is back at transparency. The switching from absorption state back to transparency occurs at high speed. This is due to the ultra fast transition of carriers between the valence band and deep states in the bandgap of the modulator active region **54a**. Consequently, the optical signal, as indicated at **55**, output from the modulator **52** can be modulated at ultra-high speeds by application of a high speed reverse bias voltage.

Fig. 6 shows an experimental graph **56** of the extinction ratio between switching the modulator between the transparency (zero bias) and absorption (reverse bias) state . The graph **56** shows an 11.8dB reduction in optical signal intensity, as indicated at **60**, when the reverse bias voltage is applied. It is to be noted that the device has not yet been optimised to give better extinction ratios, and it is believed that extinction ratios significantly better than 11.8dB should be achievable.

The novel quantum well intermixing process provides a method of regionally modifying the bandgap properties of InGaAsP quantum well structures grown on an Indium Phosphide substrate. This technique is particularly applicable to 1.3 $\mu$ m and 1.55 $\mu$ m integrated optoelectronic devices, where selected regions of the quantum well structure may require bandgap blue shifting and/or deep states for reducing carrier lifetime.

Furthermore, the technique produces bandgap modifications to selected components (e.g. modulator) of an integrated device without introducing unwanted affects to neighbouring component(s) (e.g. DFB laser). Using this novel quantum well intermixing technique, the modulator section of an integrated DFB laser/electro-absorption modulator device exhibits fast switching times with efficient optical coupling between the DFB laser and modulator region. This method of bandgap engineering enables the fabrication of efficient and compact high speed integrated optoelectronic devices suitable for 1.3 $\mu$ m and 1.55 $\mu$ m telecommunication applications. The 1.55 $\mu$ m operating wavelength region is considered a global standard for leading edge long haul fibre optic communication system. Consequently, the described QWI method is potentially suited for developing future high speed optoelectronic devices.

It should also be mentioned that whilst this alternative aspect of the present invention, where a Helium-Plasma stream provides vacancy defects is related to methods for fabricating Indium Phosphide based optoelectronic devices, it may also be applicable to GaAs based devices, although this has not been performed experimentally.